



IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF:

Takeshi Kusudou et al.

: GROUP ART UNIT: 1713

SERIAL NO: 10/616,982

: EXAMINER: Judy M. Reddick

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FOR: VINYL ALCOHOL POLYMER AND PROCESS FOR PRODUCING VINYL  
ALCOHOL POLYMER

DECLARATION UNDER 37 C.F.R. § 1.132

Honorable Commissioner of Patents and Trademrks,  
Alexandria Virginia 22313-1450

Sir:

I, Takeshi Kusudou, residing at 1621, Sakazu, Kurashiki-City, Okayama Prefecture, Japan do hereby declare as follows:

I have graduated Hiroshima University, Graduate School of Engineering in March, 1994; and from April, 1994 up to date I have been an employee of KURARAY CO., LTD. and have been mainly engaged in the field of development of modification of polyvinyl alcohol and application of the polyvinyl alcohol.

I am a first-inventor in the above-identified application and am familiar with the instant technical field.

I declare that the results of Experiments I have conducted are as follows and that they are true to the best of my knowledge and belief.

In order to show that the modified polyvinyl alcohol (PVA) containing a silyl group in a molecule defined in the claims of the above-identified application is patentably distinct from those taught or suggested in Maruyama et al U.S. Patent No. 4,567,221 and Maruyama et al U.S. Patent No. 4,708,947, comparative test has been carried out under my supervision as follows.

### Experiment

In the following Experiment, the value of "P x S" of PVA, the degree of hydrolysis of PVA and the value of "(A-B)/(B)" of PVA were measured or evaluated as described below. In addition, the evaluation of viscosity stability of aqueous PVA solution, water-resistance of PVA film with inorganic substance and binding force of PVA with inorganic substance composition were carried out as described below.

#### (a) The value of "P x S" of PVA

P indicates the viscosity-average degree of polymerization of the PVA; and S is the content (mol %) of the silyl group functionalized monomer units in the PVA.

##### (i) The viscosity-average degree of polymerization (P) of the PVA

The viscosity-average degree of polymerization (P) of the PVA was measured according to JIS-K6726.

##### (ii) The content of the silyl group functionalized monomer units in the PVA (S; mol %)

Before hydrolysis, a polyvinyl ester was purified through reprecipitation with hexane-acetone so that the non-reacted silyl group functionalized monomer was completely removed from the polymer. Next, the thus-processed polymer was dried under reduced pressure at 90°C for 2 days, and then dissolved in  $\text{CDCl}_3$  to prepare

a sample to be analyzed. The sample was analyzed by the use of a 500 MHz proton-NMR device (JEOL GX-500), and the silyl group functionalized monomer unit content of PVA was thus determined.

(iii) The value of "P x S" of PVA

The value of "P x S" of PVA was calculated from the P and the S.

(b) The degree of hydrolysis of PVA

The degree of hydrolysis of PVA was measured according to JIS-K6726.

(c) The value of "(A-B)/(B)" of PVA

A indicates the silicon atom content (unit: ppm) of the PVA, B indicates the silicon atom content (unit: ppm) of the PVA that has been washed with sodium hydroxide-containing methanol and then washed through Soxhlet extraction with methanol where the silicon atom content is based on the total weight of the PVA.

(i) The silicon atom content (unit: ppm) of the PVA (A)

The silicon atom content of PVA was determined by ashed a sample of PVA and the use a Jares Ash's ICP spectrophotometer IRIS AP.

(ii) The silicon atom content (unit: ppm) of the PVA (B)

First, 10 parts by weight of a sodium hydroxide-containing methanol solution was added to one part by weight of a sample of PVA to such a degree that the molar ratio of sodium hydroxide to the vinyl alcohol monomer units of the PVA is 0.01, then boiling the resulting mixture for one hour and separated the polymer through filtration. The washing operation was repeated five times. Next, the washed the sample of PVA was fed to Soxhlet extraction and refluxed with methanol for one week. Using the subjecting thus-washed sample of PVA and a Jares Ash's ICP spectrophotometer IRIS AP, the silicon atom content (unit: ppm) of the PVA (B) was

determined.

(iii) The value of " $(A-B)/(B)$ " of PVA

The value of " $(A-B)/(B)$ " of PVA was calculated from the A and the B.

(d) Viscosity stability of aqueous PVA solution

An aqueous solution of 8% sample of PVA was prepared and left in a thermostat at 10°C. Immediately after the temperature of the aqueous PVA solution has reached 10°C and after 7 days, the viscosity of the solution was measured. The viscosity of the aqueous PVA solution after 7 days is divided by the viscosity thereof immediately after its temperature has reached 10°C (after 7 days/immediately after the temperature control). From the data, the PVA tested was evaluated according to the criteria mentioned below.

A: Less than 1.5 times.

B: From 1.5 times to less than 2.5 times.

C: From 2.5 times to less than 4.0 times.

D: 4.0 times or more, but PVA did not gel.

E: PVA lost fluidity and gelled.

(e) Water-resistance of PVA film with inorganic substance

An aqueous 4% sample of PVA solution was prepared, to which was added an aqueous dispersion of 20% colloidal silica (Nissan Chemical Industry's Snowtex ST-O) in such a manner that the solid content-based ratio by weight of PVA/colloidal silica may be 100/10, and the resulting mixture was cast at 20°C to form a film having a thickness of 40µm. The film was heated at 120°C for 10 minutes, and then cut to give a test piece having a length of 10 cm and a width of 10 cm. The test piece was dipped in distilled water at 20°C for 24 hours, and then

taken out (recovered), water having adhered to its surface was wiped away with cotton gauze, and its wet weight was measured. After thus measured, the wet test piece was dried at 105°C for 16 hours, and its dry weight was measured. The wet weight of the test piece is divided by the dry weight thereof, and this is a degree of swelling (times). From it, the PVA tested was evaluated according to the criteria mentioned below.

A: Less than 5.0 times.

B: From 5.0 times to less than 8.0 times.

C: From 8.0 times to less than 12.0 times.

D: 12.0 times or more, but the test piece dipped in distilled water could be recovered.

E: The test piece dipped in distilled water could not be recovered.

(f) Binding force of PVA with inorganic substance composition

Silica (Mizusawa Chemical Industry's Mizukasil P78D) and 0.2%, based on the weight of silica, of a dispersant (Toa Synthetic Chemical Industry's Aron T40) were dispersed in water by the use of a homogenizer to prepare an aqueous dispersion of 20% silica. To the aqueous silica dispersion, added was an aqueous 10% sample of PVA solution in such a manner that the solid content-based ratio by weight of silica/PVA may be 100/30, and a necessary amount of water was added thereto to prepare a silica-dispersed PVA solution having a concentration of 15%.

The silica-dispersed PVA solution thus obtained was applied onto the surface of woodfree paper, using a wire bar. Its amount applied to the paper was 60 g/m<sup>2</sup> in a basic weight. Thus coated, the paper was dried with a hot air drier at 100°C for 3 minutes. This was a coated test sample. After dried, the amount of the coating layer on the paper (test sample) was 11 g/m<sup>2</sup>.

Using an IGT printability tester, the sample was tested under a printing pressure of 50 kg/cm<sup>2</sup>. The printing speed (cm/sec) at which the surface of the test sample has peeled was read, and this indicates the surface strength of the test sample. From it, the binding force of PVA tested herein was evaluated according to the criteria mentioned below. In testing the sample with the IGT printability tester, used was IGT Pick Oil M (by Dai-Nippon Ink Chemical Industry), and a mechanism of spring drive B of the tester was employed.

A: 260 cm/sec or higher.

B: From 220 cm/sec to lower than 260 cm/sec.

C: From 180 cm/sec to lower than 220 cm/sec.

D: From 140 cm/sec to lower than 180 cm/sec.

E: Lower than 140 cm/sec.

#### Experiment 1

(Producing PVA1 that corresponds to PVA used in Examples 1 to 4 and Example 8 of Maruyama et al U.S. Patent No. 4,567,221)

2275 parts of vinyl acetate, 370 parts of methanol and 855 parts of methanol solution containing 2% by weight of vinyltrimethoxysilane were fed into a 6-liter separable flask equipped with a stirrer, a temperature sensor, a dropping funnel and a reflux condenser, purged with nitrogen with stirring, and then heated up to 60°C. To this was added 20 parts of methanol containing 0.6 parts of 2,2'-azobisisobutyronitrile, and the polymerization was initiated with it. From the start of the polymerization, 51.5 parts of methanol solution containing 2% by weight of vinyltrimethoxysilane was added to the reaction system and the polymerization was continued for 4 hours and then stopped. At the time when the polymerization was stopped, the solid concentration in the system was 26.0%. Next,

methanol vapor was introduced into the system to expel the non-reacted vinyl acetate monomer from it. This gave 40% polyvinyl ester-containing methanol solution.

To the 40% polyvinyl ester-containing methanol solution, added were methanol and methanol solution containing 10% by weight of sodium hydroxide in that order with stirring so that the molar ratio of sodium hydroxide to the vinyl acetate units in the polyvinyl ester could be 0.03 and the solid concentration of the polyvinyl ester could be 30% by weight. In that condition, hydrolysis of the polyvinyl ester was started at 40°C.

With the progress of the hydrolysis, a gel was formed and it was taken out of the reaction system immediately after its formation. Then, this was ground, and 1 hour after the start of the hydrolysis, this was neutralized with methyl acetate added thereto to obtain PVA swollen with methanol, and then dried at 65°C for 16 hours to obtain PVA1.

The vinyltrimethylsilane unit content of the thus-obtained PVA1 was 0.5 mol %, the degree of hydrolysis thereof was 99.2 mol %, and the degree of polymerization thereof was 1600. The value  $(A-B)/(B)$  obtained according to the method of determining the silicon atom content of PVA1 was 80.5/100.

The PVA1 did not completely dissolve in water. Therefore, the evaluation of viscosity stability of aqueous PVA solution, water-resistance of PVA film with inorganic substance and binding force of PVA with inorganic substance composition could not be carried out.

#### Experiment 2 to 14

(Producing PVA2 to PVA14; PVAs that correspond to PVAs used in Examples 6, 7, 9 to 12, 14 and 15 of Maruyama et al U.S. Patent No. 4,567,221, and PVAs that

correspond to PVAs used in Examples 17 to 20, 38 to 40 and 42 to 45 of Maruyama et al U.S. Patent No. 4,708,947)

Various PVAs (PVA2 to PVA14) were produced in the same manner as that for PVA1 except that the amount of vinyl acetate and methanol to be fed, the type and the amount of the silyl group functionalized monomer to be fed, the amount of the polymerization initiator to be used were varied as in Table 1, and the polymerization condition and the hydrolysis condition were varied as in Table 2. The analytic data of the thus-obtained PVAs are shown in Table 3. The evaluation of viscosity stability of aqueous thus-obtained PVAs solution, water-resistance of thus-obtained PVAs film with inorganic substance and binding force of thus-obtained PVAs with inorganic substance composition are also shown in Table 3.

PVA2: It corresponds to the PVA used in Example 6 of Maruyama '221.

PVA3: It corresponds to the PVA used in Example 7 of Maruyama '221.

PVA4: It corresponds to the PVA used in Example 9 and Example 10 of Maruyama '221.

PVA5: It corresponds to the PVA used in Example 11 and Examples 20 to 24 of Maruyama '221.

PVA6: It corresponds to the PVA used in Example 12 of Maruyama '221.

PVA7: It corresponds to the PVA used in Example 14 of Maruyama '221.

PVA8: It corresponds to the PVA used in Example 15 of Maruyama '221.

PVA9: It corresponds to the PVA used in Example 17 of Maruyama '947.

PVA10: It corresponds to the PVA used in Example 18 and Example 38 of Maruyama '947.

PVA11: It corresponds to the PVA used in Example 19 and Example 39 of



Maruyama '947.

PVA12: It corresponds to the PVA used in Example 20 and Example 40 of Maruyama '947.

PVA13: It corresponds to the PVA used in Examples 42 to 44 of Maruyama '947.

PVA14: It corresponds to the PVA used in Example 45 of Maruyama '947.

Table 1

Type of PVA	Initial Feeding		Silyl Group-Having Monomer			
			Type	MeOH solution Concentration (%)	Amount of Initial Feed <sup>1)</sup>	Amount of Additional Feed <sup>1)</sup>
	VAc <sup>1)</sup>	MeOH <sup>1)</sup>				
PVA1	2275	370	VMS	2.0	855	51.5
PVA2	2450	506	vinyltriisopropoxysilane	4.0	544	36.8
PVA3	2450	314	VMS	2.0	736	50.0
PVA4	2275	365	VMS	4.0	860	51.8
PVA5	1400	1573	VMS	2.0	527	39.5
PVA6	1400	1424	vinyltriethoxysilane	2.0	676	51.0
PVA7	2450	474	vinyltriethoxysilane	2.0	576	39.0
PVA8	2450	597	vinyltriisopropoxysilane	4.0	453	30.8
PVA9	2100	927	VMS	2.0	473	35.5
PVA10	1225	1814	VMS	2.0	461	41.5
PVA11	2450	315	VMS	1.0	735	50
PVA12	2625	485	VMS	1.0	393	24
PVA13	1225	1889	vinyltriethoxysilane	4.0	361	38
PVA14	2100	934	vinyltriisopropoxysilane	4.0	466	35

VMS: vinyltrimethoxysilane

1) Parts by weight

Table 2

Type of PVA	Initiator			Polymerization Condition			Hydrolysis Condition		
	Type	Amount of Initial Feed <sup>1)</sup>	Amount of Additional Feed <sup>1)</sup>	Polymerization on Temperature (°C)	Polymerization Time (hr)	Solid Conc. (%)	Solid Conc. (%)	molar ratio	NaOH
PVA1	AIBN	0.6	-	60	4.0	26.0	30	0.03	
PVA2	AIBN	0.9	-	60	4.0	31.6	30	0.008	
PVA3	AIBN	0.9	-	60	4.0	31.4	30	0.02	
PVA4	AIBN	0.6	-	60	4.0	26.4	30	0.02	
PVA5	AIBN	1.3	-	60	4.0	20.0	35	0.03	
PVA6	AIBN	0.8	-	60	5.0	20.0	35	0.025	
PVA7	AIBN	0.9	-	60	4.0	31.4	30	0.02	
PVA8	AIBN	0.9	-	60	4.0	31.6	30	0.008	
PVA9	AIBN	1.2	-	60	4.0	29.9	30	0.02	
PVA10	AIBN	1.5	-	60	5.0	21.0	35	0.02	
PVA11	AIBN	0.9	-	60	4.0	31.2	30	0.02	
PVA12	AIBN	0.7	-	60	4.0	29.9	30	0.02	
PVA13	AIBN	1.7	-	60	6.0	24.6	35	0.008	
PVA14	AIBN	0.8	-	60	5.0	30.1	30	0.02	

AIBN: AIBN: 2,2'-azobisisobutyronitrile

1) Parts by weight

Table 3

Type of PVA	Viscosity-average degree of polymerization of PVA (P)	Content of the silyl group functionalized monomer units in PVA (S; mol%)	Degree of Hydrolysis (mol%)	P x S	(A-B)/(B)	Viscosity stability of PVA aq solution	Water-resistance of film with Inorganic Substance	Binding force
PVA1	1600	0.5	99.2	800	80.5/100	- 2)	- 2)	- 2)
PVA2	1750	0.3	88	525	62.5/100	- 2)	- 2)	- 2)
PVA3	1750	0.4	98.5	700	71.9/100	- 2)	- 2)	- 2)
PVA4	1500	1.0	98.5	1500	85.2/100	- 2)	- 2)	- 2)
PVA5	700	0.5	99.0	350	78.9/100	D	- 1)	- 1)
PVA6	700	0.5	98.5	350	75.4 /100	D	- 1)	- 1)
PVA7	1750	0.2	98.5	350	58.9/100	D	- 1)	- 1)
PVA8	1750	0.25	85.0	437.5	59.2/100	- 2)	- 2)	- 2)
PVA9	1300	0.3	98.5	390	60.7/100	D	- 1)	- 1)
PVA10	550	0.5	98.5	275	74.6/100	D	- 1)	- 1)
PVA11	1750	0.2	98.5	350	55.2/100	D	- 1)	- 1)
PVA12	2000	0.1	98.5	200	53.2/100	D	- 1)	- 1)
PVA13	500	0.5	88	250	61.1/100	C	- 1)	- 1)
PVA14	1300	0.3	98.5	390	60.7/100	D	- 1)	- 1)

1) Uniform aqueous solution with inorganic substance could not be prepared.

2) PVA did not completely dissolve in an aqueous solution.

I, the undersigned declarant, declare further that all statement made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and; further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001, of Title 18, of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 7 day of February, 2005

Name: *Takeshi Kusudou*  
Takeshi Kusudou